U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Cryogenic Fluids Density Reference System: Provisional Accuracy Statement (1980)

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CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM:
Provisional Accuracy Statement (1980)

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The improved Density Reference System, the reference densimeter, and the method of determining sample density are described.

The uncertainty of the density reference system is ± 0.055%. The contribution from the estimated systematic error in density was ± 0.022%. The estimated uncertainty caused by random error is three times the standard deviation of 0.011% and is based on sixty-three measurements of the densities of saturated liquid methane. The total density uncertainty is taken to be the sum of the systematic and random errors. This applies to the density range of 400 to 480 kg/m^3 at pressures from 0.8 to 4 bar absolute and temperatures between 109 and 128 K. This accuracy statement is expected to apply over ranges of at least 400 to 1000 kg/m^3 in density, 77 to 300 K in temperature, and 0.8 to 7 bar in pressure though the accuracy over these ranges has not been verified.

ˑ Compared to the original, this improved density reference system has greater accuracy, speed, reliability, and flexibility.

Key words: densimeter; density reference system; liquid methane; LNG.

1. INTRODUCTION

In an earlier report [1], we described the density reference system (DRS) used to test some commercially available densimeters in liquefied natural gas (LNG). These tests involved comparing the density measurement by the densimeter under test to the density measured by our DRS densimeter in an equilibrated liquid sample. This earlier report gives an estimate of the uncertainty associated with a density measurement by the DRS densimeter used as standard for comparison. The uncertainty of a single determination of the density at the instrument under test was taken to be ± 0.076%. This includes a systematic error of 0.028% and a random error of 0.048% which is three times the estimated standard deviation of 0.016%. Four different commercial densimeters were tested and the results reported [2]. The major problem with the commercial densimeters divulged by these tests and some later measurements was the calibration of the commercial instrument by the manufacturer. None of the factory calibrations were entirely suitable at LNG temperatures at the time of these tests.

Because of this calibration problem, we offered a calibration service through "transfer standards." We calibrate a manufacturer's instrument, which is then installed in a calibration system at his plant and used to calibrate instruments he builds. He would then periodically return the transfer standards for recalibration. The process would eventually yield data on the stability as a function of time of the instruments used as transfer standards. The manufacturer's calibration system and methods can be evaluated by testing in the DRS some of the instruments calibrated by the manufacturer.

The DRS sample container used in the tests of these first four commercial densimeters was designed around the densimeters tested. The densimeters in some cases were specially built. The first version of the DRS was too inflexible to deal with any design modifications of the commercial densimeters.

A more flexible sample container dewar system has been constructed and is in current use in densimeter evaluation and calibration work. This DRS design with a companion liquid sample storage dewar should be suitable for a commercial calibration facility. We find this sample container more temperature stable than that of the original DRS. The new DRS is described in more detail in Section 2.1. Safety considerations made necessary when using combustible gases are detailed in Section 2.2.

The DRS densimeter has been modified several times before, during and since the rebuild. Details of these modifications and a shift in the measured density after the rebuild are discussed in Section 3, along with the other measuring devices.

In Section 4, the measurement process is discussed. The associated systematic errors are identified, their magnitudes estimated and the overall error estimate of a density measurement is given. This estimated deviation of the density for one measurement from the true value is ± .055% for pure methane at the normal boiling point. The maintenance of this accuracy is discussed in Section 5.

Since the improved version of the DRS was completed, a number of additional commercial densimeters have been tested. Each test consisted of a series of measurements in pure liquid methane, then about 5% propane and 1% to 2% nitrogen are added to simulate an LNG mixture and another series of measurements was made. This mixture was used because both propane and nitrogen can be added without any danger of solids forming in the fill line since both have freezing points below 110 K. Measurements in an LNG-like fluid permit LNG densimeters to be tested in a fluid around the temperature and density in which they will be used. The tests in liquid methane provide a fluid with a known temperature density relationship, provided 99.97% pure methane is used, to which the DRS density value can be compared. Also, the methane density data along with the LNG like-liquid density data provide a much wider range of densities for determining the calibration equation for the instruments under test.

2. DESCRIPTION OF THE IMPROVED DENSITY REFERENCE SYSTEM

This improved DRS operates on the same principle as the original. Densimeters under test are compared to the density reference system densimeter in a very nearly isothermal liquid sample. The DRS densimeter is an Archimedes type densimeter consisting of a single crystal silicon float weighed while immersed in the sample liquid by an electronic balance. Density measurements are made over an approximately 15°C temperature range along the saturation curve of the sample liquid. The measurements are made with the sample at equilibrium after a change of sample temperature has been affected either by a liquid nitrogen cooling coil or an electrical resistance heater. The sample equilibrium is obtained by stirring the liquid with a turbine pump. Equilibrium conditions

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remain for the period of time required for measurement without stirring because the heat leak to the sample has been reduced to a small value with radiation shields and other heat flux interrupting devices.

2.1.   Sample Container

A schematic of this improved DRS is shown in Figure 1. The sample container consists of a 25.4 cm OD, 1.6 mm wall stainless steel tube extending 760 mm down from an ambient temperature stainless steel flange to a 3 mm thick dished bottom head. A similar stainless steel vessel or vacuum jacket 35.6 cm OD forms an outer wall enclosing the sample container. The space between these two vessels contains radiation shields and is maintained at a pressure below 10^{-3} pa by an oil diffusion type vacuum pump. All the stainless steel to stainless steel joints are heliarc welded. All flanges and other gasketed joints in both the insulating vacuum jacket and sample container employ "O" ring seals. Unlike the sample container of the original system, which required a low temperature indium wire vacuum seal to close it, all demountable seals on the new DRS are located at ambient temperature. A 73 mm high aluminum ring, clamped between the sample vessel and vacuum jacket flanges provides six 38 mm ID flange covered access ports into the vacuum space. Through these flanges pass the liquid nitrogen line to the various cooling coils and the gas vent lines from these coils shown in Figure 1 and the electrical leads for heaters and thermo-couples. The connection to the vacuum pump is also through one of these ports. All lines and leads are such that they can be readily disconnected to permit the counterbalanced dewar assembly to be lowered enough that the top flange is below the bottom of the sample space. The time to disconnect the few lines, remove the nuts from the twelve 13 mm studs clamping the sample container to the top
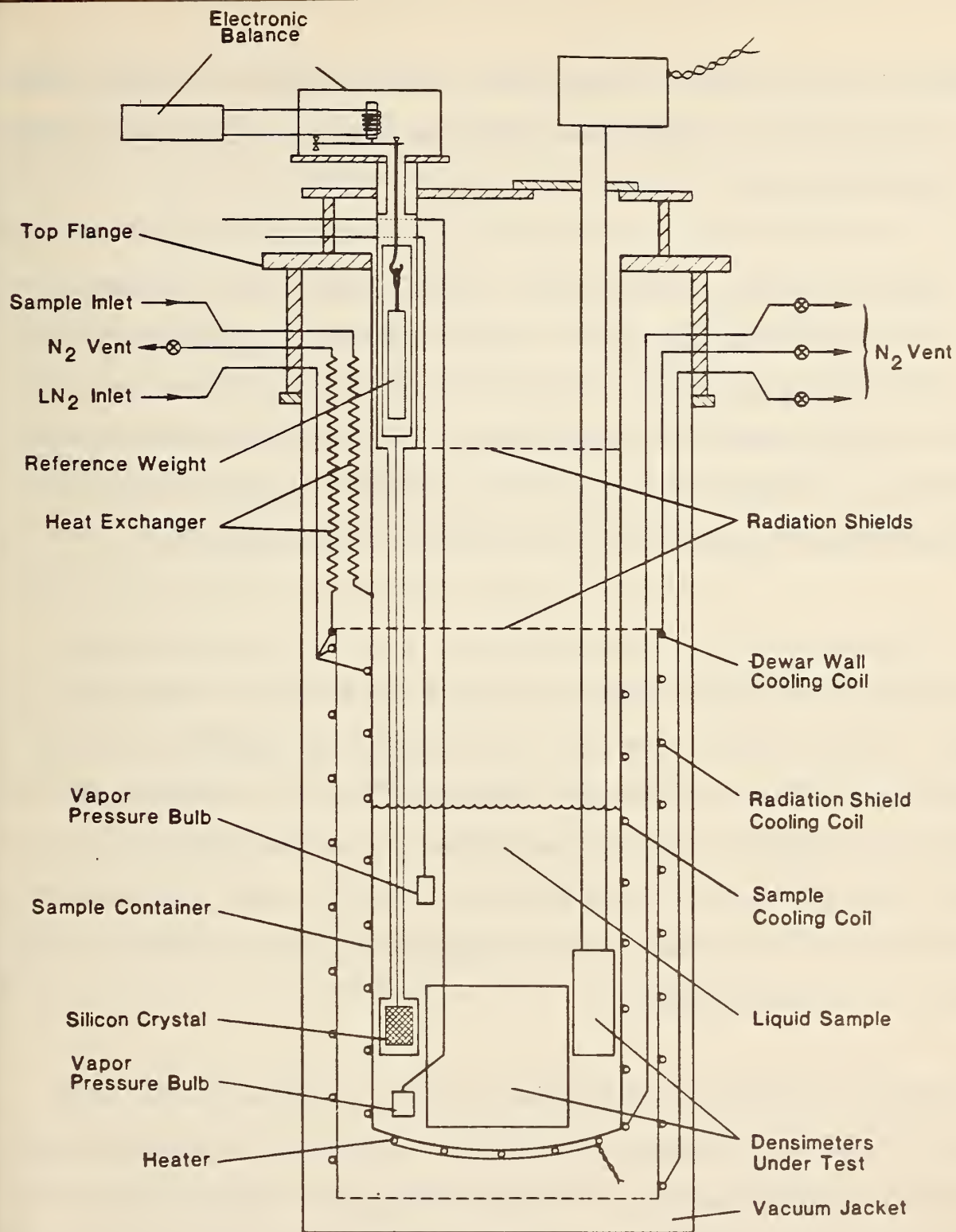
Figure 1. Schematic diagram of the improved Density Reference System.

flange and lower the dewar is a few minutes. A valve between the vacuum jacket and the vacuum line disconnect permits the dewar to be lowered without breaking the insulating vacuum.

Another 73 mm high aluminum ring is located between top of the sample container flange and the top cover of the sample container. Again, six flange covered 3.8 mm diameter access ports provide locations to introduce electrical leads, the vapor pressure bulb tubes shown in Figure 1 and for pressure gauge connections. The sample vessel seals are "O" rings. The sample pressure is maintained above atmospheric pressure in case small leaks are present.

The top plate of the sample container has a port for the DRS densimeter, a 153 mm access port shown in Figure 1 and a port for the stirrer drive shaft (not shown). The access port flange cover can be modified as required to provide mountings for various insertion type densimeters. Figure 1 illustrates the mount for a vibrating cylinder densimeter. An "O" ring sealed gland on the access flange provides a gas tight stem seal. To avoid a seal on a rotating shaft, the stirrer drive shaft is coupled magnetically from the exterior to the interior of the sample chamber.

The evacuated annular space between the sample container and the vacuum jacket contains all the refrigeration systems used to condense and maintain the sample at cryogenic temperature. All the refrigeration is supplied from an adjacent LN_2 storage dewar through a vacuum insulated transfer line into the LN_2 inlet shown in Figure 1. This inlet is connected to all the various cooling coils and the amount of cooling by each coil is regulated by throttling the independent N_2 gas vent lines from the various coils. The coil on the radiation

shield, Figure 1, is vented continuously and the temperature of this polished copper shield is maintained below the sample temperature. In Figure 1, the dewar wall cooling coil attached to the shield mounting ring a few centimeters above the sample level is maintained at a temperature a few degrees above the sample temperature to minimize the heat conducted down the sample vessel wall. Within the sample vessel, a copper radiation shield, with an aluminum foil shield on top, interrupts the heat radiated down from the top of the sample holder. A second radiation shield is placed a few centimeters above the lower shield. The operating temperature of the lower shield is normally a few degrees above the liquid temperature. The cooling coil and heater on the sample vessel, Figure 1, are used only to change the sample temperature.

The sample is condensed into the DRS from gas bottles using liquid nitrogen via the counterflow heat exchanger shown in Figure 1. This parallel tube heat exchanger, composed of two 8 mm I.D. copper tubes about 7 m long soft soldered together along their length, will condense the 16 liters required in the sample holder in about an hour. The actual time depends on the LN_2 supply rate. Most joints in these coils and lines are soft soldered and all coils and heaters are soft soldered to the surfaces to which they transfer heat.

Each time the density of an LNG or methane sample is measured, the temperatures of the sample near the top and bottom are also determined by measuring the methane vapor pressure in the vapor pressure bulbs shown in Figure 1. The vapor lines are connected through a selector valve to a quartz spiral Bourdon tube pressure gauge. The temperature difference, ΔT, measured is nearly always less than 20 mK and usually less than 10 mK. This low temperature gradient is obtained without the low speed stirring used in the original system [1]. The temperature

drift during the measuring period is comparable in magnitude to ΔT. Temperatures of the radiation shields and the annular shield support ring, shown in Figure 1, are monitored by thermocouples to provide information for minimizing the heat leak to the sample. The temperature and pressure of the gas surrounding the reference weight are recorded and used to provide the gas buoyancy correction to this weight reading.

A system of similar design, but perhaps larger, should be suitable for a manufacturer's calibration facility. To speed up the operation, a manufacturer could employ additional cryogenic vessels into which he can transfer the calibration liquids. Heated N_2 gas or additional electrical heaters can be used to rapidly warm the sample holder to change densimeters and an LN_2 spray nozzle could be used to rapidly cool the calibration dewar, or the instruments calibrated could be introduced and removed from the top, without warming the whole dewar. Either way, some modest care is required to ascertain the dewar is properly purged and inerted before introducing a cryogenic sample.

2.2 Safety Considerations in the DRS Design

Manufacturers of densimeters suitable for cryogenic use have demonstrated some reluctance to employ calibration methods using cryogenic liquid combustible gases. In this section, we discuss safety considerations incorporated by NBS in the DRS.

An experimental system using combustable gases can be made safe by eliminating any opportunity for a combustible mixture of air and the gas to form, or by eliminating all ignition sources in any area combustible mixtures form. The

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elimination of combustible mixtures is the preferred way to make a system safe. Thus, the DRS sample handling system is gas tight and evacuated before introducing the combustible gas. However, should a leak develop in the system or an accident occur, a combustible mixture could result so ignition sources have been minimized in the laboratory. Since one can never be assured that ignition sources are completely eliminated, the probability of a combustible mixture forming from an accident and the lifetime of such a mixture, if formed, is minimized by a laboratory exhaust fan. This fan has the capacity to change the room air about every 12 minutes.

The schematic of the combustible gas handling system for the DRS shown in Figure 2 illustrates the essential safe handling features. All lines that may or do involve gas exhausting from the sample container are connected to a stack that vents above the roof of the building. The sample container, approved for operating pressures to 10 bar, has a 10 mm ID relief line connected to the vent with a relief valve set just above the highest operating pressure. In the very unlikely event that the sample vessel ruptures and dumps the contents of the sample into the vacuum jacket, a 25 mm diameter relief line ducts the resulting vapor through a low pressure relief valve to the vent. The vacuum pumps maintaining the insulating vacuum also exhaust to the vent line. The vessel vacuum pump exhaust is connected to the vent because the system fill procedure requires the vessel to be evacuated, filled with the sample gas, then evacuated and filled twice more before condensing the sample. When the tests are completed, the liquid is blown through valve 5, Figure 2, via evaporating coils. The gas remaining is pumped out and the sample container is back filled with N_2 gas during warmup. This pump also serves to purge the gas sample supply lines when changing or starting gas supplies. Valve 6, Figure 2, provides a route to

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DRS Combustable Gas Handling System

Figure 2

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release sample gas into the vent. Check valves could be placed in both the valve 5 and 6 lines to preclude air entering the sample container if these valves should be accidentally opened with lower than atmospheric pressure in the sample container. The solenoid valve 12 prevents complete loss of vacuum in the event of a power failure.

The liquid sample is often left in the sample container overnight unattended. Liquid nitrogen is passed through the sample and radiation cooling coils at a rate sufficient to remove the heat leak to the sample. The vapor pressure is held at about 1½ bar absolute by a feedback system that senses this pressure and supplies sufficient additional heat to the sample heater, Figure 1, to maintain the set pressure.

Small quantities of gas escaping from the DRS would be swept out of the room by the ceiling vent fan. To reduce the chances of igniting any larger spill, mainly "explosion proof" electrical equipment operates in the room during tests. The stirrer motor case is purged with compressed air. All the electrical cabinets are enclosed and purged with compressed air. Access to the laboratory is limited and since the floor is conducting, conducting shoes or ground straps are used by anyone regularly in the laboratory. A combustion gas detector connected to a warning horn is located near the DRS.

The vapor pressure bulbs contain less than a liter of STP methane, but this can result in a very high vapor bulb pressure if not properly vented to the storage cylinder during warmup. Two bypass relief valves between the vapor bulbs and the storage cylinder eliminate this potential hazard.

3. THE DRS DENSIMETER AND INSTRUMENTATION

3.1. The Reference Densimeter

The DRS densimeter described in the Technical Note 698 [1] has undergone several modifications since that report was prepared. A major modification occurred when the electronic balance used to weigh the single crystal was replaced.

3.1.a. The Densimeter with the Original Balance

Since manually disconnecting and connecting the silicon single crystal and reference weight caused occasional discontinuities in the electrical balance reading, pneumatic drive cylinders were connected to both actuators. These cylinders were mounted on the scale case and were sufficiently slow moving to gently place the weights on the balance while not shaking the balance mounting. This modification decreased the scatter of the methane density values determined by the DRS relative to the Haynes-Hiza [3] density values calculated from the average sample temperature.

When the sample containment portion of the DRS was reconstructed as describ-ed in Section 2, the silicon crystal disconnect mechanism was rebuilt. The suspension wire in the vapor region was replaced by a 1.6 mm diameter thin wall stainless tube and the assembly connecting the suspension to the bottom of the balance was modified. The balance was readjusted for corner load effects. These adjustments, when properly made, make the balance weight reading indepen-dent of the position on the pan a weight is placed.

The density of methane in the new sample holder as determined by the DRS densimeter was offset by approximately 0.07% relative to the Haynes-Hiza [3] and Goodwin [4] values for the density calculated from average temperature for six subsequent methane fillings. The vapor bulb positions were altered and the methane in the bulbs changed without affecting this offset. To ascertain the pressure gauge had not shifted calibration, it was compared to the barometric pressure and found to be in agreement. The temperature difference represented by the difference between the barometric pressure and the vapor pressure gauge reading amounted to less than 0.01 K. The methane density difference corresponding to 0.01 K is too small for the DRS densimeter to measure. This offset will be discussed in more detail below.

3.1.b.   Addition of a New Balance

Recently an electronic balance with sufficient range to directly weigh the 128 g crystal to 1 mg has become commercially available. This balance has other advantages; it is more compact and much less sensitive to vibration than the original balance. It is lightweight and can be transported in any orientation without securing the moving parts. The DRS densimeter has been rebuilt to incorporate one of these electronic balances. Conceptually, and in actual design, this densimeter differs little from the original densimeter. However, because it has sufficient capacity to weigh the silicon directly, a reference weight [1] with the attendant buoyancy correction is no longer required. We have retained the reference weight as a means of calibrating the balance and monitoring the calibration during tests.

A suspension system consisting of two cages, one for a reference weight and one for the silicon crystal, is attached to the underside of the balance. The reference weight cage is about 20 cm below the balance and in the sample gas space while the silicon crystal cage is 76 cm below the balance and completely immersed in the sample liquid. The section of the suspension passing through the liquid surface is a wire. The suspension is always attached to the balance. Lifting mechanisms permit the weights to be attached and detached from the suspension independently. Surface tension effects on the suspension should cancel since weight off (zero) readings are included in the measurements and subsequent density calculations.

The liquid density ρ is now given by the relation (equation 4, Reference 1) with M_a replaced by $(M_a - M_{ao})$:

$$\rho = \rho_s \quad \frac{1 - (M_a - M_{ao})}{M_s} \tag{1}$$

where ρ_s is the silicon density, M_s is the silicon crystal mass in vacuum, M_a is the apparent mass when weighed in the liquid and M_{ao} is the balance reading with the crystal and reference weight disconnected. This latter value nearly always is zero to $\pm$ 1 mg as the balance is tared (zeroed) with the silicon crystal removed before the density readings are taken.

The systematic offset in the observed density of liquid methane compared to Haynes-Hiza discussed in section 3.1.a remained and even increased slightly with the introduction of the new balance. The reference 1 data are probably in error because of an undetected corner loading error in the balance. We cannot directly confirm this supposition since we cannot recover the old balance adjustment.

Because of the way the silicon crystal and the reference weight were placed on the balance in the original system, any corner loading error must have had some effect on density measurement. The reference weight was placed on the pan and the crystal was suspended from a part of the balance assembly well below the pan. This vertical offset in attachment points probably did not contribute a systematic error to the density determination, but the relative displacement in the horizontal plane of the attachment points that existed could affect the results. We placed 100 g weights on the pan which were weighed relative to a counterweight such that the balance reading was on scale on the 20 g range of the balance. However, the pan was only corner load adjusted so 20 g could be read to within a milligram, thus a mass value error approaching 5 mg at the edge of the pan was possible for a 100 g weight even for a properly adjusted balance. The results of a series of tests of the balance indicated some corner loading error was still present even after the balance was readjusted.

Comparison tests between the DRS densimeter and a silicon crystal densimeter built for a commercial calibration facility showed agreement to about 0.01%. These results are shown in Appendix 9.1 and lend added support to the contention that the systematic shift in the measured methane densities relative to the measurements reported in Reference 1 resulted from an error in the adjustment of the original electronic balance.

In some later tests, a third silicon densimeter, the Portable Reference Densimeter (PRD) was compared to the DRS densimeter in the DRS [5]. The PRD and DRS densimeters are similar in design, but the silicon single crystal was obtained from a different source. The density readings were indistinguishable.

3.1.c. Calibration of the Balance

Even though the present DRS densimeter no longer requires a reference weight to determine LNG density, we have retained this weight for calibrating the balance and monitoring the calibration. The balance is calibrated by weighing the reference weight in air and adjusting the balance to read the apparent true mass in air. The reference weight still weighs approximately the same as the silicon crystal when the latter is submerged in liquid methane.

In the course of taking data at each sample temperature setting, this reference weight is measured and recorded. The apparent mass is corrected for gas buoyancy and compared to the true mass value. This correction is readily made for methane or methane-nitrogen samples but not for methane-propane-nitrogen samples because propane suppresses the methane vapor pressure by an uncertain amount and because the gas mixture is slow to reach equilibrium. The method of calculating the buoyancy correction is detailed in Appendix 9.3. The reference weight is located in a region in which the gas temperature is -10 to -20°C, which contributes to the buoyancy correction uncertainty in the ternary mixture even though the gas temperature is measured and applied to the buoyancy calculation.

The reference weight is weighed periodically in air to monitor the balance calibration. The calibration can be adjusted if needed, or a calibration factor can be introduced. In the six months of operation, the calibration has not been adjusted. A calibration correction amounting to 1.7 mg was included in the calculations for two fillings. For later fillings, a correction was not needed. The results of monitoring the reference weight during tests are presented in Section 4.

Corner loading errors are unlikely in the new silicon crystal weighing system since both the reference weight and the silicon weight are suspended below and placed on the suspension axial to the suspension wire, thereby eliminating essentially all possibility of corner loading errors.

3.2. Sample Temperature

Temperature is measured using vapor pressure thermometers. One thermometer bulb was located at the bottom of the sample volume and the other near the top. Each thermometer contains a few cm^3 of liquid methane. Pressure communicates from each thermometer bulb via a 1.6 mm O.D. stainless capillary tubing through a selector valve to a quartz-spiral bourdon tube pressure gauge. The temperature range used is 110 K to 126 K. The accuracy of the quartz-spiral gauge is 0.01% of full-scale pressure as determined by a master piston gauge calibrated by NBS. This pressure uncertainty is equivalent to 0.01 K at 110 K and 0.003 K at 125 K.

3.3. Sample Vapor Pressure

The liquid sample vapor pressure was measured using a bourdon tube pressure gauge with a 0 to 4 bar range and an 0.2% of full scale accuracy according to the manufacturer. The vapor pressure is used only for a small buoyancy correction to the reference weight and need not be accurately known.

4. MEASUREMENT PROCESS PARAMETERS

4.1. Bounds for Systematic Errors

The primary sources of uncertainty in the density measurements can be obtained from examination of the measurement equation. The knowledge of the basic uncertainties of the separately measured quantities such as the masses and densities, can be combined to give an estimate of the systematic errors in the density as measured by the density reference system.

Equation (1), the measurement equation, gives the density ρ as a function of several independently measured variables.

$$\rho = \rho(M_s, M_a, M_{ao}, \rho_s, T). \tag{2}$$

The temperature is included here because the density at the test densimeter is the quantity we wish to know and a temperature gradient may exist.

The uncertainty in ρ, arising from uncertainty in some variable x, for example, can be evaluated from

$$\delta\rho = \frac{\partial\rho}{\partial x} \; \delta x \tag{3}$$

The total uncertainty in density is taken to be the square root of the sum of the squares of the various contributions,

$$\frac{\delta\rho}{\rho} = \frac{1}{\rho} \left[\Sigma \left(\frac{\partial\rho_i}{\partial x_i} \; \delta x_i \right)^2 \right]^{1/2} \tag{4}$$

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This is the propagation of error relationship for systematic error when the variables are independent and the magnitudes of the relative errors are small so that second order terms are negligible [6].

Table 1. Systematic errors

Variable, x	$\partial\rho/\partial x$	Max Magnitude*	δx	$\delta\rho/\rho$ (%)*
M_s	$(\rho - \rho_s)/M_s$	-0.015 cm^{-3}	0.0005	0.0019
M_a	$-\rho_s/M_s$	-0.0184 cm^{-3}	0.001 g	±0.0046
M_{ao}	ρ_s/M_s	0.0184 cm^{-3}	0.001 g	±0.0046
ρ_s	ρ/ρ_s	0.17	6×10^{-5} g/cm^3	±0.0026
T	$\partial\rho/\partial T$	0.0016 g/cm^3 K	0.05 K	±0.02
total, from equation (4)				$\pm0.022\%$

*At the smallest measured density, ~0.4 g/cm^3.

Table 1 is a summary of the most significant contributions to the total systematic uncertainty in density as estimated from the various contributing sources. The first column, labelled x, identifies the variable for which the uncertainty is calculated. The second column is the partial derivative of the liquid density with respect to the variable of the first column and the third column gives its maximum magnitude. The column labelled δx is the estimated largest error of that variable.

The systematic error, δx, of M_s, is estimated from the standard deviation of the weighings and the uncertainties of the 5 weights used (Appendix 9.2). The estimate of the systematic error for M_a and M_{ao} is the resolution of the electronic

balance or ± 1 mg. The calibration of the electronic balance is monitored by
weighing the reference weight as discussed earlier which permits holding this
uncertainty within the balance resolution. The error estimate of the silicon
crystal density covers uncertainties due to the temperature and pressure effects
(Appendix 9.6) as well as uncertainties in published densities (Appendix 9.7).

The combined temperature gradients and drift during data acquisition
measured by the vapor pressure thermometers rarely exceed the value of 0.05 K.
We assume for the purposes of error estimation a ΔT no larger than 0.05 K. This
temperature difference is dependent on the heat input of the instruments under
test and ΔT is usually less than half this value. A density difference resulting
from this temperature difference can be calculated from the methane properties
[3,4].

Average System

Temperature	$\Delta\rho/\rho$ for $\Delta T = 0.05$ K
110 K	0.017%
127 K	0.02%

These uncertainties are the same size as claimed for the original DRS and
are most certainly overestimated. To confidently reduce these values, however,
we would prefer to have a more detailed knowledge of the temperature distribu-
tion in the sample during a density measurement. Our present accuracy needs do
not warrant increasing the complexity of the system by the addition of more
thermometers. An additional systematic error results from the uncertainty in
the absolute value of T. This is not included in the table since it makes no

contribution to the systematic error when densimeters are being compared. When liquid methane density measurements are being compared with those of other workers, however, we have a 0.01% contribution to the systematic error at 110 K that decreases to less than 0.001% at 127 K.

4.2.   Calculation of the Random Uncertainty for the DRS

The accuracy and precision of the DRS densimeter is essentially independent of liquid composition. Its accuracy and precision depend primarily upon the accuracy and precision of its balance and how well the weight and density of the silicon crystal are known. The ability to make an accurate reading will, of course, depend upon conditions within the sample holder. The liquid needs to be relatively quiet, well mixed and of a fairly uniform temperature in the area in which the densimeters are being tested. It should be sufficient, then, to test the DRS densimeter in a liquid whose density is known. Saturated liquid methane was chosen as its density, as a function of temperature, has been determined by Goodwin [4] and Haynes and Hiza [3], and it is the major constituent of LNG.

The present evaluation of the improved DRS is based on data taken for fifteen fillings of the liquid sample holder. Ten of these fillings were made after the new balance was installed; so we will be looking at the continuity of the DRS through a balance change.

The major interest in commercial densimeters is their performance in an LNG-like mixture. We first fill the DRS sample holder with liquid methane, take a series of measurements over the range of about 110 to 125 K, then add nitrogen (about 1% to 2%) and propane (about 4% to 6%) to simulate LNG and take another

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series of measurements in the same temperature range. We then have data comparing the DRS densimeter to the Haynes-Hiza methane densities and an evaluation of the densimeter under test in an LNG-like mixture.

We compare the values of density as determined by the Haynes-Hiza method for saturated liquid methane and the corresponding values determined by the DRS densimeter. The vapor pressure bulbs, from whose average value the Haynes-Hiza density is calculated, bracket the volume containing the silicon crystal. The Haynes-Hiza value, then, is more of an average reading, while the DRS densimeter registers a point value.

A continuing calibration test of the new DRS balance is made as discussed in Section 3.1.c. The silicon crystal apparent mass in the sample liquid is 100 g to 107 g for the mixtures being considered, and the mass value of the reference weight is approximately 103 g. This weight is used before filling the system, during the density measurements, and after the system is emptied to determine the calibration of the DRS balance.

Figure 3 is a plot in chronological order of the differences between the Haynes-Hiza values for saturated liquid methane and the corresponding values determined by the DRS densimeter. The symbols alternate from filling to filling to distinguish the separate fillings. The measurements in the first five fillings, counting the groups from the left, were by the old DRS balance after readjusting it for corner loading. The jump between the fourth and fifth filling is attributed to a change in the calibration of the balance since the densimeter had been dismantled and reassembled between these fillings.

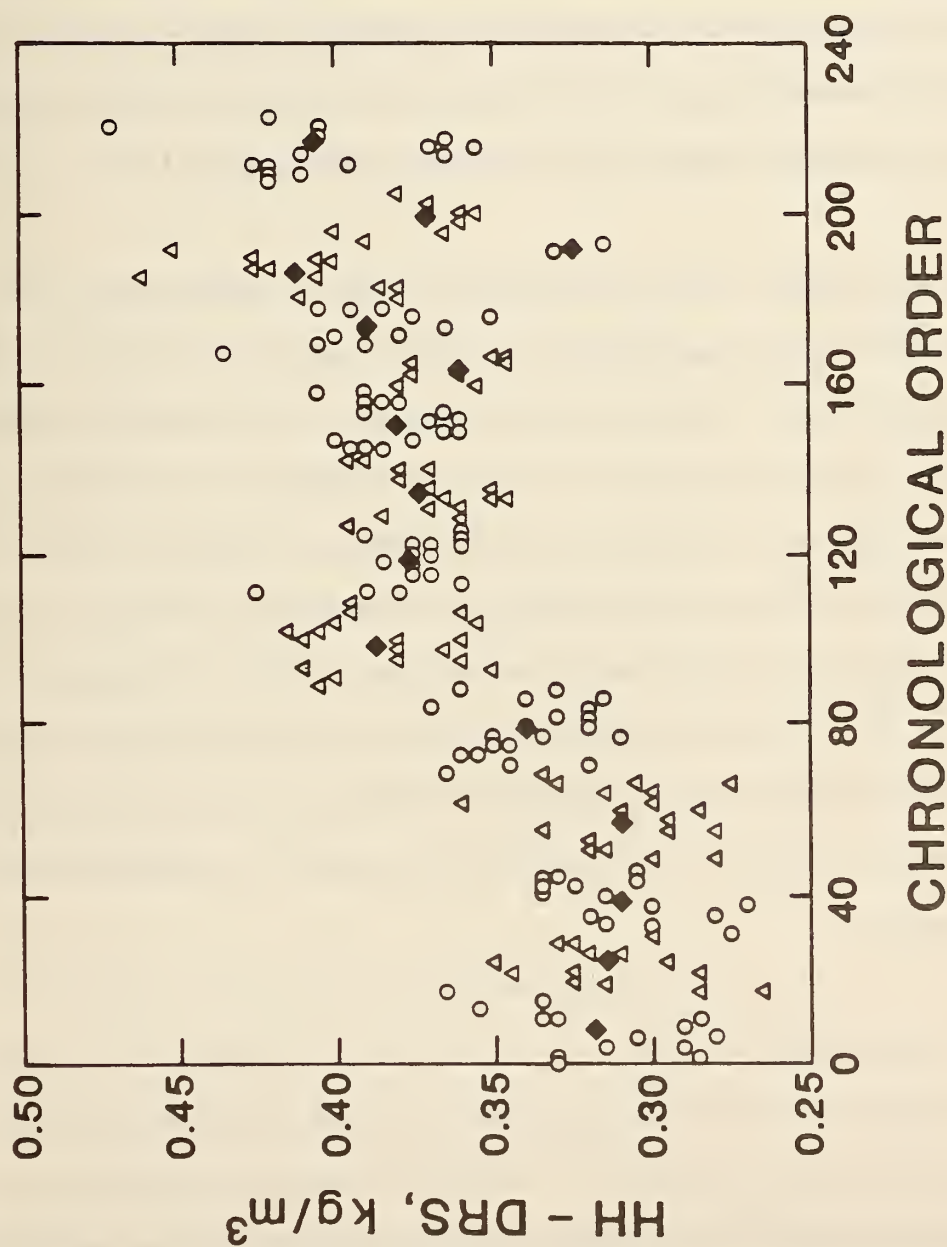Figure 3. Difference between the liquid methane density measured by the DRS and that calculated from the average temperature using the Haynes-Hiza results as a function of chronological order. All the methane data for the time period April 1979 through February 1980 are shown. The symbols alternate between circles and triangles to show separate fillings. The solid diamonds show the averge difference for each filling.

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The apparent shift occurring after the installation of the new DRS balance probably results from some remaining corner loading effects for the old balance as discussed in Section 3.1.b.

The average difference between the Haynes-Hiza and the DRS densimeter values using the new balance is approximately 0.09% larger than the 0.01% difference reported in Reference [1]. The difference for the old balance readjusting was approximately 0.07% larger than previously reported [1].

The average difference between the methane densities determined by the Haynes-Hiza method and those determined by the DRS densimeter show the latter to be approximately 0.1% lower. That the DRS densimeter is now measuring density correctly is supported by the data for fillings 11 through 14. The meter under test for these fillings was also an Archimedes densimeter using a silicon crystal. See Appendix 9.1 for details of this comparison. The average difference between the corresponding density values given by this meter and the DRS densimeter is .004% ± .017% (95% C.I), i.e., the density values were not statistically distinguishable. The comparison between the DRS and Portable Reference Densimeter, to be reported later, also shows the present DRS densimeter to be correctly measuring the density.

Each time a commercial densimeter was tested in pure methane, data were taken to permit comparing the DRS measured density to the Haynes-Hiza density calculated from the average temperature. A series of density measurements with each liquid sample were taken over a range of temperatures by either heating or cooling the sample to a target temperature, waiting for equilibrium while stirring the sample, and taking the desired schedule of readings with the

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stirrer off. The target temperature was only nominally achieved at equilibrium. The sample was stirred again and the readings duplicated. The duplicate readings provided assurance that the DRS and test densimeters had reached equilibrium. A lack of equilibrium was never noted. The second reading also reduced the chance of losing a data point through a reading error or a malfunction of a test densimeter, which are often sensitive to bubbles. The temperature drift between the duplicate sets of readings for the new DRS had a standard deviation of approximately 0.1 K with the second reading averaging 0.05 K higher.

The random errors of the duplicate density values obtained from a densimeter as described above would be expected to correlate more closely with each other than with values at different temperatures. In fact, the correlation between duplicates for the difference between the Haynes-Hiza and DRS densities is about 0.5. A correlation of 1.0 would mean the duplicates provide the same information, while a correlation of 0 would mean the duplicates provide independent information on the process. Since we have much more data than needed for the error estimate and the correlation between the duplicate data at each temperature complicates the analysis, only the first of each duplicate reading has been used to analyze the DRS.

The model used to analyze the methane data is:

$$H(T) - Y(T)_{ij} = \mu(T) + \alpha_i + e_{ij} \qquad (5)$$

where $Y(T)_{ij}$ is the jth density determination by the DRS on the ith methane filling for temperature T; H(T) is the corresponding density value derived from the Haynes-Hiza relationship, $\mu(T)$ represents any systematic difference between

the two methods at temperature T, α_i represents a shift in the mean for measure-
ments on the ith filling, and e_{ij} the random contribution to the jth measurement
made on the ith filling.

The solid diamonds in Figure 3 show the average difference for each filling
and show the shifts, α_i in the mean of the Y_{ij} from one filling to the next.
Considering the data before the new balance, the only significant shift is
between the 4th and 5th fillings, and this probably resulted from dismantling
the densimeter in between the two fillings. The data taken after the installa-
tion of the new balance show the shifts from filling to filling to be rather
small for the first five fillings, but somewhat larger for the last five. The
α_i appear to be random in nature and have an estimated standard deviation of
.013 kg/m^3(.0031%). A 99% upper confidence bound for this value is .036 kg/m^3
(0.0082%). What accounts for the shifts in the α_i is at present unknown. The
deviations of the measured values of the calibration weight from the true mass
value of 102.9022 g, ΔW, are shown versus chronological order in Figure 4. A
buoyancy correction must be made to the balance reading to obtain the true mass
value (see Appendix 9.3). The changes in the mean of the observed true mass
values of the calibration weight from filling to filling are statistically signi-
ficant, but they are not well correlated with the α_i, and if they were, their
estimated standard deviation could account for only a 0.0020% component in the
variation of the α_i, leaving additional effects to account for 0.0024%. A dif-
ference between the temperature of the liquid at the crystal and the average
temperature given by the two vapor pressure bulbs might also contribute to this
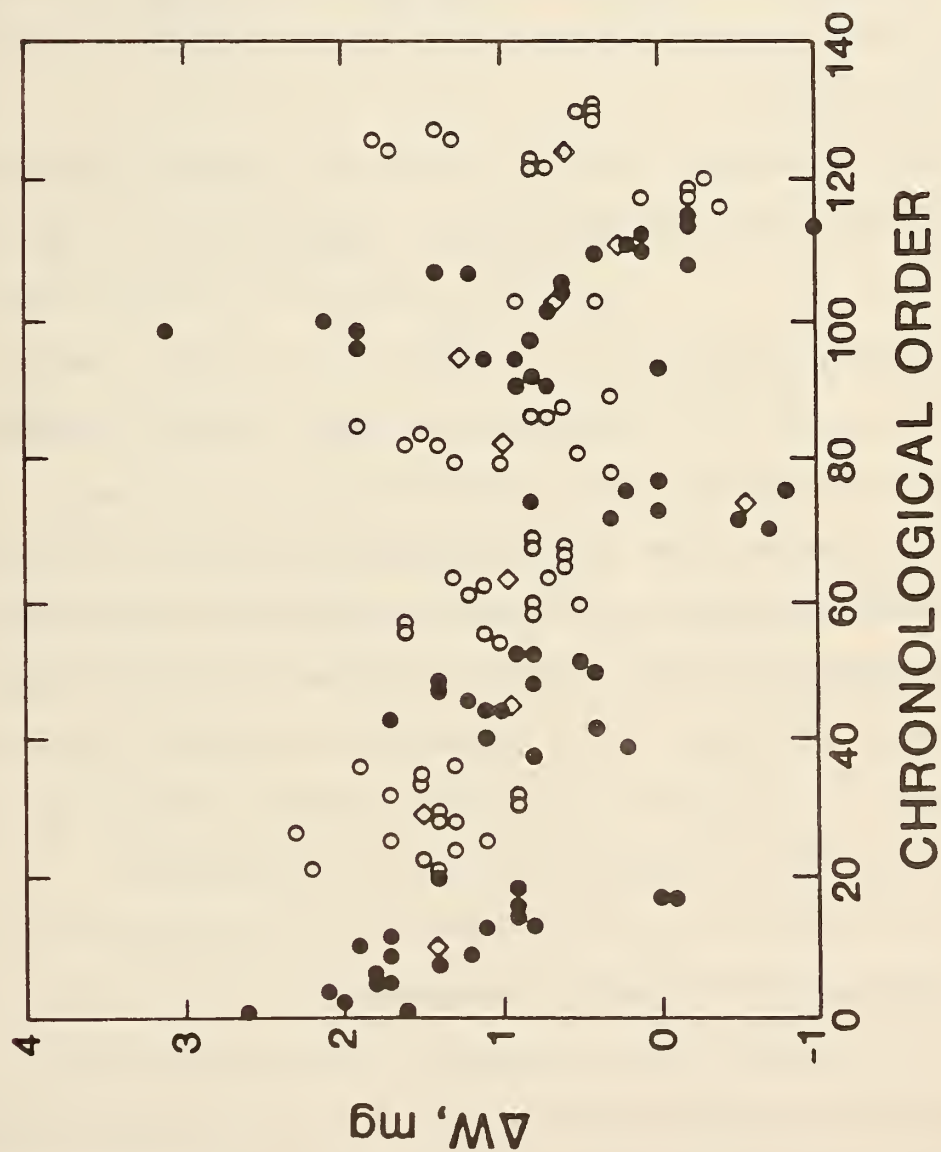uncertainty if the difference were to persist over the time of the run (filling).

Figure 4. Reference weight corrected to vacuum value measured during the tests in liquid methane compared to vacuum value determined from equal arm balance shown in chronological order. Closed and open circles differentiate fillings. The open diamonds in each filling show the average.

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Based on the differences shown in Figure 3, the within filling standard deviation for fillings through the 15th is estimated to be 0.0216 kg/m^3(.0051%) with a 99% upper bound of 0.0277 kg/m^3(.0065%).   This is a conservative estimate.

A least squares lot of the DRS density data for fillings 1 through 5 to the temperature of the saturated methane after removing the filling-to-filling shifts results in the equation,

$$D(T) = 526.935 - 0.410996\ T - .0047017T^2 \qquad (6)$$

where D(T) is the predicted density in kg/m^3 for T in kelvin.   The fit was made assuming that only the DRS density data were subject to error.   However, T being the average of the upper and lower temperature of the liquid sample, it will differ from the temperature of the liquid at the densimeter.   This assumption is likely to bias the estimated coefficients in the equation and also the estimated standard deviation for the DRS values.   The residual standard deviation is 0.027 kg/m^3 (37 degrees of freedom) and is comparable to the within standard deviation discussed above.   The range for T was 109 K to 128 K.   A similar fit for the DRS density data for fillings 6 through 15 results in the equation:

$$D(T) = 525.092 - 0.382535T - 0.0048151T^2 \qquad (7)$$

The residual standard deviation for this fit is 0.019 kg/m^3 (53 degrees of freedom).   The range for T was 109 K to 130 K.   The differences between the predicted values of the two equations over the range 110 K to 130 K is given for selected temperatures in the table below.   The last column of the table gives the differences less the 0.07 kg/m^3 estimated offset between the old balance values and the new balance values.

Temperature	Equation 6	Equation 7	Eq. 6 - Eq. 7	Less 0.07
110	424.83	424.75	.08	.01
115	417.49	417.42	.07	.00
118	412.97	412.91	.06	-.01
120	409.91	409.85	.06	-.01
125	402.10	402.04	.06	-.01
130	394.05	393.99	.06	-.01

The percentage deviation, $100 (H(T) - D(T))/D(T)$, between the Haynes-Hiza relationship [3] and equation (7) is shown in Figure 5. The same comparison is also shown for equation (7) and the Goodwin results [4].

4.3. Uncertainty Statement

The use of three times the estimated standard deviation is commonly used in reporting the limits of random error. This derives partly from simplicity and partly from the fact that if the true standard deviation were being used,

$$m(T) \pm 3 \text{ SD}$$

would contain 99% (almost all) of the measured $Y(T)_{ij}$, where $m(T)$ is the systematic error. Section 3.1 gives bounds to this value of ± 0.022%. From Section 3.2, the filling-to-filling standard deviations 99% upper bound is 0.036 kg/m^3 and that for within a filling has a 99% upper bound of 0.028 kg/m^3. Combining these two to obtain an upper bound on the standard deviation of a single determination of Haynes-Hiza minus DRS, we get $((.036)^2 + (.028)^2)^{1/2} = .046$ kg/m^3. Although this value contains the uncertainty for
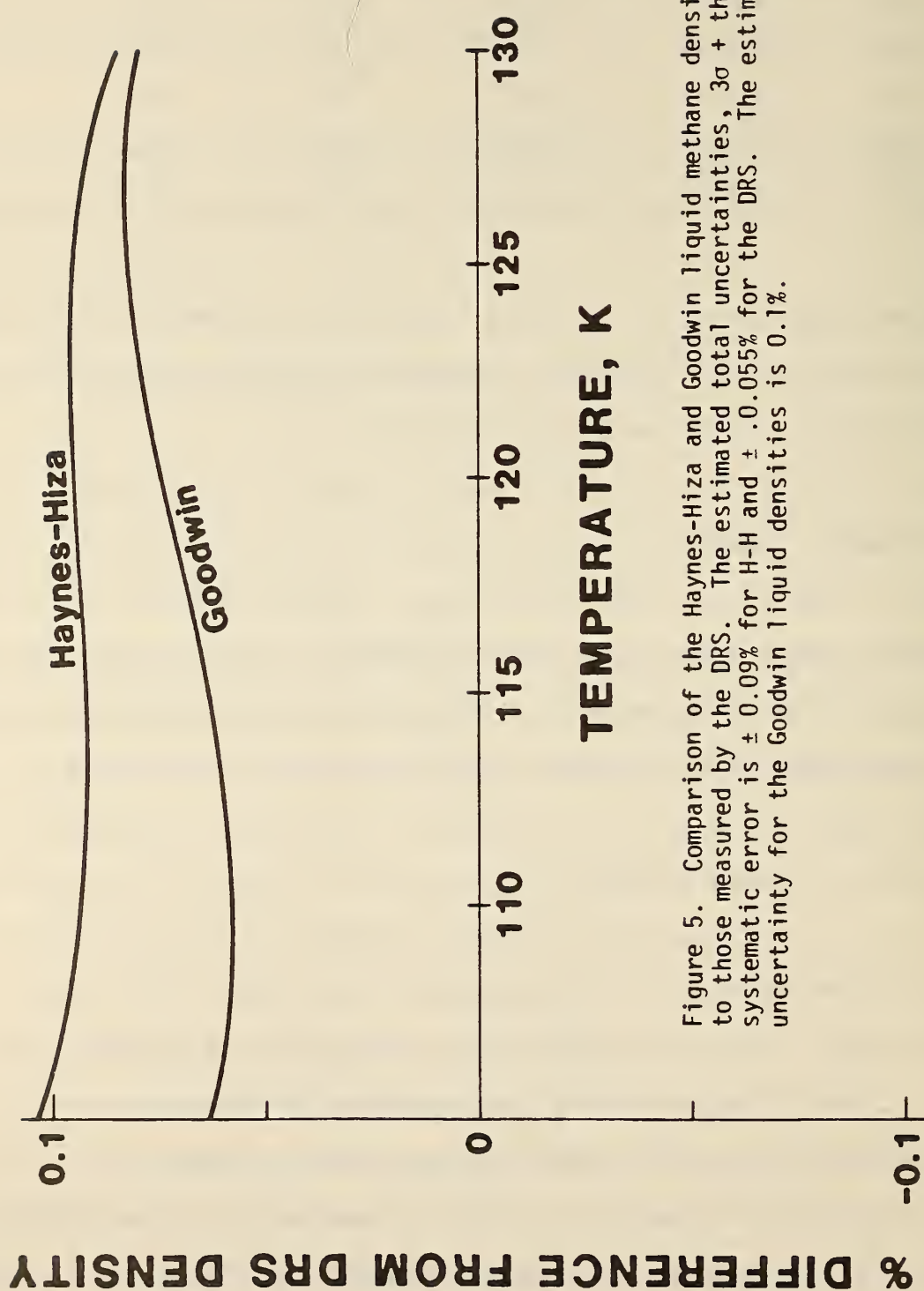
Figure 5. Comparison of the Haynes-Hiza and Goodwin liquid methane densities to those measured by the DRS. The estimated total uncertainties, 3σ + the systematic error is $\pm$ 0.09% for H-H and $\pm$ .0.055% for the DRS. The estimated uncertainty for the Goodwin liquid densities is 0.1%.

both density determinations (Haynes-Hiza and DRS), we are assigning all of it to the DRS. The 3σ value for this uncertainty is 0.138 kg/m^3.

Transforming the estimated standard deviaton of ± 0.046 kg/m^3 to percent at 422.63 kg/m^3, the normal boiling point density of methane, gives a value of ± 0.011%. The sum of 3 x 0.011% plus 0.022% gives the present estimated limit of total uncertainty for a single density measurement made on pure methane with the DRS as ± 0.055%. This uncertainty decreases for LNG mixtures because of the increased density.

5. MEASUREMENT PROCESS CONTROL

As future measurements are made, the random errors will be continually monitored and the systematic error estimates will be confirmed experimentally as described below.

Each time a set of density reference measurements is made using the system, measurements on at least two separate fillings of pure liquid methane will be included in the tests. Density measurements will be made at temperatures around 110 K, 115 K, 120 K and 125 K with some randomness in the order. The remeasured methane densities will be compared to the Haynes-Hiza results and to the earlier reference system measurements to determine whether the system has shifted. This reliability of the system will be checked only in conjunction with density comparison work rather than periodically because of the expense of making density measurements. The reference weight, of course, now permits a continuing monitoring of the balance performance and can provide information to

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correct any drift within a run. The methane tests will primarily monitor the silicon crystal itself and the vapor pressure bulb thermometer performances.

For future occasions, the within standard deviations will be compared statistically to those of previous occasions to test for any change in this measure of precision. We will also test for the presence of occasion-to-occasion shifts or signs of non-random behavior (e.g., drifting). If there are no apparent changes, the data from previous occasions will be combined with the new data to obtain updated estimates. Any statistically verifiable changes in the DRS process will call for corrective action with respect to the process. Revised uncertainty statements will be presented as needed.

6. SUMMARY

The density reference system of the National Bureau of Standards, is described. The procedure for determining the density from weighing, zeroing and calibrating the balance and the calculational method is discussed.

The uncertainty of the improved density reference system for pure methane at the normal boiling point is ± 0.055%. The contribution from the estimated systematic error in density was ± 0.022%. The estimated uncertainty caused by random error is three times the standard deviation of 0.011% and is based on sixty-three measurements of the densities of saturated liquid methane. This

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total density uncertainty is taken to be the sum of the systematic and random errors and should vary approximately as ρ_m/ρ where ρ_m is the density of normal boiling point liquid methane and ρ is the density of the sample liquid.

7. ACKNOWLEDGMENTS

The authors wish to thank W. G. Stewart and J. D. Bruel of this laboratory for their design work on the DRS densimeter and their help with the rebuilding of the density reference system.

8. REFERENCES

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[2] Siegwarth, J. D., Younglove, B .A., and LaBrecque, J. F., An Evaluation of Commercial Densimeters for Use in LNG. NBS Technical Note 697, October 1977.

[3] Haynes, W. M., Hiza, M. J., Measurements of Orthobaric Liquid Densities of Methane Ethane, Propane, Isobutane and Normal Butane, J. Chem. Thermodynamics $\underline{9}$, 179, (1977).

[4] Goodwin, R. D., The Thermophysical Properties of Methane, from 90 to 500 K at Pressures to 700 Bar. NBS Technical Note 653, April 1974.

[5] J. D. Siegwarth and J. F. LaBrecque, A Portable Calibration Densimeter for use in Cryogenic Liquids. NBS Technical Note 1035, to be published.

[6] Cook, N. H., and Rabinowitz, E., Physical Measurement and Analysis, Addison-Wesley Publishing Co., Inc., 1963.

9. APPENDICES

9.1. A Comparison of the DRS Densimeter and an Industrial Reference Densimeter

9.1.a. Introduction

An industrial densimeter calibration facility, similar to the Density Reference System (DRS) of the National Bureau of Standards, is presently under construction. Like the DRS, the calibration method consists of simultaneous density measurements of a homogeneous liquified natural gas-like liquid by the densimeter under test and a reference or calibration densimeter.

The industrial reference densimeter, hereafter referred to as the IR densimeter, for this industrial facility and the density reference system densimeter are Archimedes type densimeters. Both densimeters consist of silicon

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single crystals immersed in the sample fluid and weighed by electronic balances. The main difference between the densimeters is the choice of electronic balance as will be discussed below. Neither densimeter requires calibration in a fluid of known density since the calibration is determined from the weight and volume of the silicon single crystals. Thus, none of the parameters used to determine density from the weighing of the crystal are adjustable for either densimeter and we are comparing the densimeters, rather than calibrating either. In this appendix, we present the results of a comparison between the DRS and IR densimeters in the Density Reference System. These results show that within the specified uncertainty of the DRS densimeter, no significant difference exists between these reference densimeters. However, the accuracy of the calibration of other densimeters calibrated by the IR densimeter must be based on an analysis of the accuracy of the whole calibration facility and not just the IR densimeter.

9.1.b. Industrial Reference Densimeter

The method of calculating density from a measurement by the IR densimeter is similar to the method described in Reference 1 (main text). Because the conventional read out unit of the electronic balance was replaced by a digital volt meter to increase sensitivity, the calibration was not adjustable and the read out did not give grams directly. An additional small brass mass is weighed to obtain a scale factor. This scale factor is applied to the difference between the reference weight and the immersed silicon crystal.

The density equation is:

$$\rho = (z(M_{ao} - M_a) + M_s - M_w + M_w \rho_g / \rho_w) / (M_s / \rho_s).$$

This equation and the symbols are identical to equation (7) of Reference 1 with substitution of the gas buoyancy correction; but there, $z = 1$. Thus M_{ao} is the balance reading for the reference weight, M_a is the reading for the immersed silicon single crystal, M_w and M_s are the true mass values of the reference weight and silicon crystal and ρ_g, ρ_w, and ρ_s are the densities of the sample vapor in the vicinity of the reference weight, the reference weight and the silicon crystal at 110 K respectively. The quantity z has been introduced because the balance is uncalibrated. A calibration weight of about 10.3 g is weighed and this value is divided into the true mass value of the calibration weight reduced by the amount of the mass of the gas displaced i.e., the apparent mass value. The value for z was nominally 1.002 in this work. The silicon apparent mass was read twice. The reference weight apparent mass was recorded between each weighing so four values of $M_{ao} - M_a$ were obtained and averaged. A similar procedure was used to weigh the calibration weight in gas.

The true mass values of the weights M_s, M_w, and M_c, where M_c is the calibration weight used in the calculations, are:

$$M_s = 163.7952 \text{ g}$$
$$M_w = 132.7430 \text{ g}$$
$$M_c = 10.3172 \text{ g}$$

These values have an uncertainty of about ± 1 mg which produces an uncertainty of 0.003% for liquid methane density. Since these weights were determined on an equal arm balance, no gravitational constant corrections are required.

The required densities are:

$$\rho_s = 2.33078 \text{ g/cm}^3 \text{ (silicon at 110 K)}$$
$$\rho_w = 8.4 \quad\;\; \text{g/cm}^3 \text{ (Brass at ambient temperature)}$$

and ρ_g is determined as described in Appendix 9.3.

The weighing was done with an 0.1 mg sensitivity beam balance using a set of class S weights. The various weights were transposition-weighed, and buoyancy was corrected. These weights should be periodically checked to assure the values do not change with use due to chipping, scratching, oxidation, dirt, etc.

Even though the silicon crystal is large and thus provides more sensitivity, this electronic balance is less sensitive than that in the DRS and the weighing method is inferior so the measurement uncertainty is greater. The electronic balance in the IR densimeter is capable of measuring weights of 0 to 400 g, but its resolution is only ± 10 mg when equipped with the factory readout unit. A resolution of about 1 mg was sought using a more sensitive digital volt-meter is substituted for the factory readout. The method of comparing the crystal weight in liquid to a reference weight was used, though the accuracy of this method compared to a direct weighing of the crystal was not examined. The direct weighing method had a disadvantage in these measurements because a capacitor placed across the analog output of the balance to reduce the noise level resulted in a long system time constant. The accuracy of the density measurements by the IR densimeter are also affected by the accuracy of the required gas bouyancy corrections to the reference weight and the small scale calibration weight. The method of calculating this buoyancy correction is detailed in Appendix 9.3.

9.1.c.   Results

    The two reference densimeters were compared in four separate fillings.
More of the data were taken in pure methane on the first test because the refer-
ence weight came off the manipulator during the LNG tests.   The second test was
principally for demonstration so the LNG like mixture data were taken mainly for
the last two tests.   On the third test only two methane readings were made.

    Figure 9.1 shows the percentage differences

$$\delta\% = \frac{(\rho_{IR} - \rho_{DRS}) \times 100}{\rho_{DRS}} \quad (\%) \qquad (9.1)$$

versus run number where ρ_{DRS} and ρ_{IR} are the densities measured by the DRS and
IR densimeters respectively.   The different symbols in the figure refer to
composition: 0 for methane and Δ for the LNG-like mixture.   The corresponding
solid symbols represent the arithmetic averages of the δ% for the two liquids
from filling to filling.   The solid-dot line connects methane averages, and a
dotted line connects the LNG averages.

    The most striking feature of Figure 9.1 is that the averages of δ% for the
first two methane tests are higher than for the last two.   This is also true
with regard to the LNG tests but to a lesser extent.   It is also evident that
for the first two tests the methane averages were higher than the corresponding
LNG averages.   We cannot say now whether this pattern is part of the random
changes that can be expected in the operation of this system, or whether there
are some learning effects in the operation of a new densimeter since these are
the first measurements made with this industrial reference densimeter.   For the
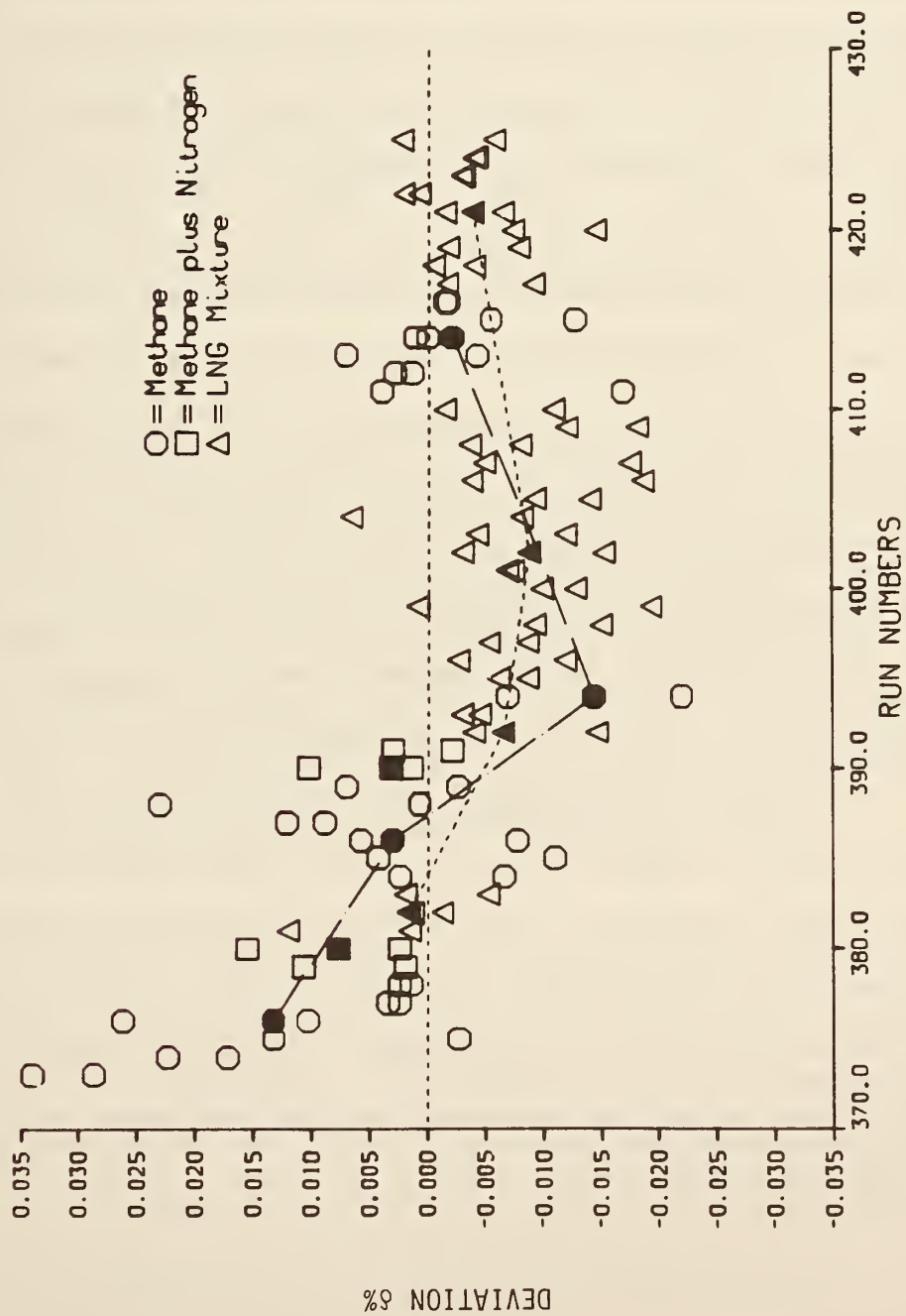
Figure 9.1. Percentage diffenence between the IR and DRS Densimeters versus Run Number.

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purposes of this report, the changes in the average values of the $\delta\%$ from filling to filling are assumed random. Also the $\delta\%$ for methane are sufficiently different from those for LNG for the data for the two liquids to be analyzed separately.

Two kinds of random uncertainty are considered in this analysis: random errors that individually affect the $\delta\%$ within a filling, and errors which affect the mean (long term average) of the $\delta\%$ from filling to filling. The standard deviation within fillings is designated by σ_E and that for filling-to-filling by σ_F. The following table gives estimates of σ_E, σ_F and the mean for three comparisons: ρ_{IR} versus ρ_{DRS}, ρ_{HH} versus ρ_{DRS}, and ρ_{HH} versus ρ_{IR}, where ρ_{HH} is the density of the saturated liquid methane according to the work of Haynes and Hiza and is based on the average temperature in the sample holder. The estimates for σ_E are based on 39 observations, while the estimates for σ_F are based on the four averages of the $\delta\%$ for the four fillings. Percentages are based on normal boiling point of methane of 422.63 kg/m^3. The analysis of the methane data shows essentially no difference between the mean for ρ_{IR} and the mean for ρ_{DRS}. The within filling standard deviation for $100\,(\rho_{IR}-\rho_{HH})/\rho_{HH}$ is 0.01% which is the same value as for the percentage difference for $\delta\%$, but the percentage difference for $100\,(\rho_{HH}-\rho_{DRS})/\rho_{DRS}$ is only half that, i.e., 0.005%. This indirect comparison suggests that the within standard deviation for ρ_{IR} is significantly larger than for ρ_{DRS}. This may be attributable to the types of weighing systems employed in the two densimeters. Looking at the σ_F column we see little difference for the three comparisons. This might indicate that the magnitude of whatever affects the mean value for one densimeter is the same as that which affect the other.

Table 9.1. Statistical Summary for Percentage Differences for Methane Data (%)

δ%	Estimate of σ_E	Upper 95% confidence limit	Estimate of σ_F	Upper 95% confidence limit	95% Confidence interval for mean
$\dfrac{\rho_{IR}-\rho_{DRS}}{\rho_{DRS}} \times 100$	.010	.012	.0085	.034	-.0037±.017
$\dfrac{\rho_{HH}-\rho_{DRS}}{\rho_{DRS}} \times 100$	.0051	.0063	.0063	.022	.087±.012
$\dfrac{\rho_{HH}-\rho_{IR}}{\rho_{IR}} \times 100$	.010	.013	.0071	.032	.083±.015

The estimated values of σ_E and σ_F for δ% equation (9.1) in the case of the LNG-like mixture are, respectively, 0.005% and 0.004%. The first of these numbers is based on 60 observations and the second on the means of the four fillings. A 95% upper limit for σ_E is 0.006% and a 95% upper limit for σ_F is 0.014%. The 95% confidence interval for the mean of the δ% for the four fillings of LNG is -0.006% ± .009%. Based on the data for either methane or LNG, there is no significant offset between the two densimeters.

The measured value of the reference weight, corrected for buoyancy, was occasionally more than a milligram different during these tests from its assigned mass value of 102.9022 g. The average value for the methane runs is 0.8 mg higher and that for the LNG runs is 0.5 mg lower than this value. Some of the deviation is probably due to non-equilibrium in the sample vapor space so the correction for buoyancy has detectable errors, and there seems to be some

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error in the buoyancy correction itself. Over the course of the measurements, the reference weight true mass values show no evidence of change in the calibration of the DRS balance.

9.1.d. Summary

The IR and DRS densimeters agree to within the limits of statistical error. Except for perhaps a slightly larger random error for the IR densimeter, we see no practical difference between the two densimeters.

When the IR densimeter is used to calibrate other densimeters in some other calibration device, other factors besides the reference densimeter uncertainty are important and may even dominate. For instance, the degree to which the liquid sample in the calibration system is homogeneous and isothermal during the comparative density measurement is very important. From the measurements reported here, we can only report an uncertainty relevant to insertion in the DRS. An uncertainty statement including the system in which the IR densimeter is to be used is required to estimate the accuracy to which another densimeter may be calibrated. The portable reference densimeter is available to do this [5].

9.1.e. References

References in section 8.

9.2 True Mass of the Silicon Single Crystal

The weight of the crystal has been determined by weighing the crystal against a set of class S stainless steel weights on an equal arm balance with a

0.1 mg resolution. Since the weighings are in air at ambient temperature and the silicon density is smaller than the weights, an air buoyancy correction is required. Also, the balance arms are sufficiently unequal so that 0.6 mg must be added to the measured weight of any object of 130 g mass if weighed only on the left pan. The 99% confidence interval for the mean of the six weighings of the silicon crystal in the table below is 127.4351 ± .0003 g. A calibration certificate for the weights used appears in Appendix 9.5. The sum of the uncertainties of the S weight values for 127.390 g is added to 0.0003 g for a total silicon mass uncertainty of ±0.0005 g.

Date	Silicon Crystal Vacuum Weight
2/2/79*	127.4348
5/7/79*	127.4352
6/15/79	127.4353
8/17/79	127.4352
1/8/80	127.4349
8/22/80	127.4351
Average =	127.4351

*Weighed on left pan only with .0.6 mg added.

The true mass values of the silicon single crystal and the reference weight measured relative to the NBS standard of mass are shown on the weight certificate (following page). Our weighings on the equal arm balance at the Boulder Laboratory are within the estimated uncertainty of the certificate mass values. The true masses of these two weights will be monitored in the future using the balance and S weights at Boulder. The Boulder values of 127.4351 g and 102.9022 g for the silicon and reference weight true masses were used in this report.

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U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

WASHINGTON, D.C. 20234

REPORT OF CALIBRATION

January 23, 1981

For: J. D. Siegwarth
      Division 773.1
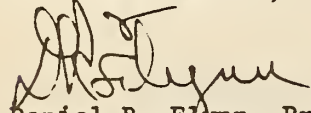   NBS - Boulder

Item: Two (2) Mass Standards
       1. Silicon single crystal: 2.329g/cm^3
       2. Copper reference standard: 8.5g/cm^3

The above items have the mass values shown with reference to the NBS
standard of mass. The volume was computed from its mass and above
density.

Item	Mass (grams)	Uncertainty (grams)	Volume at 20°C (cm^3)
Silicon	127.4345	0.0007	54.7164
Copper	102.9026	0.0007	12.1062

The uncertainty figure is an expression of the overall uncertainty using
three standard deviations as a limit to the effect of random errors of
measurement, the magnitude of systematic errors from known sources being
negligible.

For the Director,

Daniel R. Flynn, Program Manager
Mechanical Production Metrology
CMEPT/NEL

9.3 Gas Buoyancy Corrections

The gases used in these tests to make the liquid samples are methane, nitrogen and propane. Only the first two are ever present in significant amounts in the vapor space for the mixtures used if the system is at equilibrium. Some evidence suggests, however, that the propane is not necessarily at equilibrium when the LNG-like sample is first created. Lack of equilibrium is implied by the observed mass value of the DRS densimeter calibration monitoring weight which is located partially inside the dewar where the gas temperature varies between about -10°C and -30°C. A buoyancy correction using the measured gas temperature must be applied to this weight and the result compared to the true mass value to monitor the calibration. When propane is first added, the observed true mass value is low, which could result from the gas density correction being too small because propane vapor is present.

The method of determining buoyancy corrections for methane and methane ntirogen mixtures is straightforward. The density of the methane gas was calculated from the equation of state given in reference 1. This equation is:

$$P = RD + \rho^2 a + \text{(higher order terms in } \rho) \qquad (1)$$

where P is the pressure, ρ is density, R is the gas constant and T is the temperature. The coefficient of the ρ^2 term is:

$$a = N_1 T + N_2 T^{1/2} + N_3 + N_4/T + N_4 T^2 \qquad (2)$$

For the temperature and pressure range of interest and the accuracy required, the higher order terms can be neglected.

The density, ρ, in moles per liter can be derived from (1) for P in bars and T in Kelvin with R = .0831434 and:

$$N_1 = -1.8439486666 \times 10^{-2}$$

$$N_2 = 1.0510162064$$

$$N_3 = -1.6057820303 \times 10$$

$$N_4 = 8.4844027562 \times 10^2$$

$$N_5 = -4.2738409106 \times 10^4$$

This relation fits the data of Goodwin [2] in the region of T = 240 to 295 K and P = 1 to 4 bar to better than 0.1%.

When some nitrogen is added to the methane, we assume that the vapor pressure in excess of the value of pure methane at that temperature (this value is obtained from the vapor bulb readings) is contributed by the nitrogen gas and calculate gas density accordingly. The density contributed by the nitrogen gas is determined from the perfect gas relation, ρ = (.33694) P/T (gm/cc), with no virial terms, where P is the partial pressure of nitrogen in bars and T is temperature in Kelvin. This relation fits the nitrogen tables of Strobridge [3] to better than 1/2 percent over the required mixture region of 240 to 295 K and 1 to 4 bars vapor pressure.

When propane is added to the mixture, determining the density of the vapor becomes more difficult since adding propane reduces the partial pressure of methane. From some earlier density measurements in methane containing 5% propane, we could estimate the suppression of the methane vapor pressure as a function of the pure methane vapor pressure P_{CH4} to be P = $0.015P_{CH4}$ − 0.031,

where the pressures are in bars and P_{CH4} is given by the vapor pressure thermometers. This correction is only an estimate as the methane-propane-nitrogen mixture used varies somewhat from filling to filling. This correction is subtracted from the methane partial pressure and added to the nitrogen partial pressure before calculating the gas buoyancy corrections to the various weights. The concentration of propane in the vapor we consider negligible.

[1] McCarty, R. D., A Modified Benedict-Webb-Rubin Equation of State for Methane Using Recent Experimental Data, Cryogenics 14, 276 (1974).

[2] Goodwin, R. D., Thermodynamic Properties of Methane from 90 to 50 K at Pressures to 700 Bar, NBS Technical Note 953, April 1974.

[3] Strobridge, T. R., The Thermodynamic Properties of Nitrogen from 64 to 300 K between 0.1 and 200 Atmospheres, NBS Technical Note 129, January 1962.

9.4. Linearity of the DRS Electronic Balance

The linearity of the electronic balance was tested by weighing 1,2,2,4, and 100 g class S weights in combination to produce weights of 100, 101, 102, 103, 104, 105, 106 g in random order. These weights well represented the range of observed mass values encountered in the densimeter runs. In comparing the certified values of the weights (See Appendix 9.6) to those measured by the DRS balance, the linearity factor for the DRS values was calculated to be 1.000049 at 100 g with an estimated standard deviation of .000025 (12 degrees of freedom).

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The 95% confidence interval for this factor is .999995 to 1.000103. Over the six gram range, the effect may be virtually nothing to .0006 grams. Even the extreme possibility is not large enough to be considered of any real influence in the density measurements being made with the DRS so no linearity effect is included in the uncertainty estimate.

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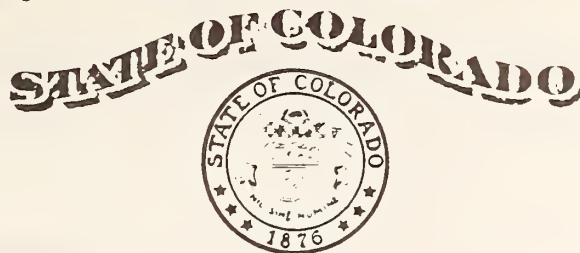
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COLORADO DEPARTMENT OF AGRICULTURE

406 STATE SERVICES BUILDING
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May 27, 1980

REPORT OF TEST

Henry Christensen, Roggen
John L. Malloy, Denver
Elton Miller, Ft. Lupton
Don Moschetti, Center
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Clede Widener, Granada
Kenneth G. Willmore, Denver

OWNER: National Bureau of Standards
Thermophysical Properties Div.
Boulder, Colorado

Certification No. 6086
S/N: NBS K-1.

DESCRIPTION: 100 g to 20 mg, Fisher weight kit.

The standards described below have been tested and compared with the
standards of the State of Colorado, and have been found to be within the tolerances
as prescribed by the National Bureau of Standards for Class S weights. The effect
of air bouyancy has been considered negligible.

ITEM	APPARENT MASS CORRECTION		UNCERTAINTY		CLASS S ADJUSTMENT TOLERANCE
100 gram	-0.0069	mg	0.1096	mg	1.200 mg
50	+0.1650		0.0786		0.12
20	+0.0470		0.0217		0.074
20•	+0.0181		0.0217		0.074
10	-0.0225		0.0197		0.074
5	+0.0002		0.0131		0.054
2	+0.0809	O/T	0.0093		0.054
2•	+0.0226		0.0093		0.054
1	+0.0398		0.0090		0.054
500 mg	+0.0146		0.0082		0.025
200•	-0.0044		0.0141		0.025
200:	-0.0059		0.0141		0.025
100	-0.0316		0.0087		0.025
50	-0.0041		0.0081		0.014
20•	+0.0089		0.0079		0.014
20:	+0.0104		0.0079		0.014

THESE CERTIFICATIONS ARE TRACEABLE TO THE
NATIONAL BUREAU OF STANDARDS.

ALL CERTIFICATES ISSUED BY THE COLORADO
DEPARTMENT OF AGRICULTURE-METROLOGY LAB-
ORATORY EXPIRE ONE YEAR FROM THE DATE OF
ISSUANCE.

F H Brzoticky, Chief Metrologist
Colorado Metrology Laboratory
3125 Wyandot St.
Denver, Colorado 80211

9.6. The Change in Volume of the Silicon Crystal for Hydrostatic Compression and Thermal Contraction

The buoyant force of the liquid on the silicon crystal will be reduced by the decrease in volume due to hydrostatic compression. This is described by

$$V = V_o(1 - kP)$$

where V_o is the volume at the reference pressure, in this case about one atmosphere or one bar. P would be the pressure in excess of this and k the compressibility;

$$k = - \frac{1}{V} \frac{\partial V}{\partial P}\bigg|_T .$$

This correction was found to be negligible since $k = 1.01 \times 10^{-6}$ bar^{-1} and at 110 K and $P \simeq 6$ bar, $\frac{\Delta V}{V} = 6 \times 10^{-6}$. In this case k was computed from silicon data on velocity of sound by McSkimmin [1] using the usual relations for bulk modulus and elastic constant as evaluated from sound velocities.

The change in volume was computed from the thermal contraction of silicon values from Gibbons [2]. We have

$$\frac{L_{298} - L_T}{L_{298}} = (25.5 \pm 0.6) \times 10^{-5}$$

for the change from 298 K to 100 K where L is length. The uncertainty, 0.6×10^{-5} is 3σ or 3/2 of Gibbon's probable error of 0.5% multiplied by 3. This value is essentially unchanged over the temperature interval 100 K to 140 K.

$$\frac{\Delta V}{V} = 3\,\frac{\Delta L}{L} \;,$$

$$\rho_s(100K) = \rho(298K)\,(1.000765 \pm 0.000018)$$

[1]   McSkimmin, H. J., Measurement of Elastic Constants at Low Temperatures by
      Means of Ultrasonic Waves--Data for Silicon and Germanium Single Crystals,
      and for Fused Silica, J. Appl. Phys. <u>24</u>, 988 (1953).

[2]   Gibbons, D. F., Thermal Expansion of Some Crystals with the Diamond
      Structure.   Phys. Rev. <u>122</u>, 136 (1958).

9.7   Densities of Single-Crystal Silicon

Densities of Silicon	Temperature	Preparation	Range of ρ_s
2.328982* g/cm^3	Ambient	Grown in vacuum	1.5 ppm
2.329022*	Ambient	Grown in Argon	1 ppm
2.32900**	25°C	No specified	± 9 ppm

*   Each are average of 12 measurements, Bowman, Schoonover, and Jones [1].
      The density given for the vacuum grown crystal in their introduction
      contains a typographical error.   Their primary interest was the variability
      of the density over each of the sample boules hence they did not specify
      precisely the crystal temperatures.

** Henins and Bearden [2] measured the density of 18 crystals from four manufacturers to a precision better than 2 ppm. The density values ranged from 2.328986 to 2.329021 g/cm³.

Based on these density measurements we assume a density halfway between the extreme values of 2.32900 ± 0.00002 g. The assumed uncertainty in silicon single crystal density spans this range. When computing ρ_s at 100 to 140 K we add the expansion correction uncertainty to this density uncertainty (Appendix 9.7) and obtain for ρ_s,

$$\rho_s = 2.33078 \pm 0.00006 \text{ g/cm}^3$$

[1] Bowman, H. A., Schoonover, R. M., and Jones, M. V., Procedure for high precision density determinations by hydrostatic weighing, J. of Research, NBS C, 71C 178 (1967).

[2] Henins, I., and Bearden, J. A., Silicon crystal determination of the absolute scale of x-ray wavelengths, Phys. Rev. 135, A890 (1964).

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Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631

13. Type of Report & Period Covered

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The improved Density Reference System, the reference densimeter, and the method of determining sample density are described.

The uncertainty of the density reference system is ± 0.055%. The contribution from the estimated systematic error in density was ± 0.022%. The estimated uncertainty caused by random error is three times the standard deviation of 0.011% and is based on sixty-three measurements of the densities of saturated liquid methane. The total density uncertainty is taken to be the sum of the systematic and random errors. This applies to the density range of 400 to 480 kg/m^3 at pressures from 0.8 to 4 bar absolute and temperatures between 109 and 128 K. This accuracy statement is expected to apply over ranges of at least 400 to 1000 kg/m^3 in density, 77 to 300 K in temperature, and 0.8 to 7 bar in pressure though the accuracy over these ranges has not been verified.

Compared to the original , this improved density reference system has greater accuracy, speed, reliability, and flexibility.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

densimeter; density reference system; liquid methane; LNG.

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